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Niobium phytic prepared from phytic acid and $NbCl_5$: Highly efficient and heterogeneous acid catalysts

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Preparation of functional catalysts using naturally-occurred building blocks is of great importance. In this work, we designed a functional heterogeneous acid catalyst, niobium phytic, using phytic acid, which could be obtained from the seeds and grains of plants, as the building block to react with $NbCl_5$. The prepared niobium phytic was characterized by XRD, FT-IR, XPS, SEM, TEM, NH_3-TPD and N_2 adsorption-desorption examinations. The niobium phytic showed very high activity for both cyanosilylation of carbonyl compounds and dehydration of carbohydrates. It was also found that niobium phytic had higher activity than commercial Nb_2O_5. In addition, niobium phytic could be easily recovered and reused without reducing the reaction activity considerably. Further study indicated that both higher acidity and lower crystallinity contributed significantly to the excellent catalytic performance of niobium phytic. The findings in this work provide the view of designing new functional catalyst using naturally-occurred building blocks for various organic reactions.

Introduction

With the increasing attention on the utilization and transformation of biomass,[1] design of efficient catalysts based on naturally-occurred building blocks has becoming a hot topic in recent years.[2] A salient feature of naturally-occurred building blocks is their diversity to provide more opportunities for designing novel catalysts with specific functions to catalyze various reactions.

Different naturally-occurred building blocks have been used to generate efficient catalysts. Among various naturally occurring compounds, amino acids are the most used compounds for the preparation of bio-based catalysts. For example, amino acids supported on polystyrene could be used as efficient catalyst for chemical fixation of carbon dioxide.[3] Cu^{II}-complexes derived from amino acids could catalyze the asymmetric oxidative coupling of 2-naphthol.[4] Amino acid ionic liquids were successfully synthesized and showed eminent catalytic activities towards Aldol reactions and the synthesis of styrene carbonate from styrene oxide and CO_2.[5] Besides amino acids, chitosan could be converted into chitosan-Schiff base complexes for aerobic oxidation of cyclohexene.[6] Recently, Guo and co-workers found that tannic acid (TA) could coordinate with Rh^{III} to form Rh^{III}-TA capsules through the chelation ability of phenolic structure, which showed excellent performance for the hydrogenation of quinolone.[7] These developments on catalyst preparation from naturally-occurred building blocks provide a wider view for designing efficient catalysts, which is interesting and attractive.

Phytic acid, a major phosphorus reservoir in plants, can be obtained from the seeds and grains of plants and widely used as a chelating agent, food additive, and antioxidant.[8] Because there are six phosphinic groups in its structure (Scheme S1), phytic acid can be used as the source of phosphoric acid to coordinate with various metal ions to form a novel metal phosphonate. Metal phosphonates are very useful functional materials, which have gained much attention owing to their diverse potential applications in adsorption, catalysis, separation, energy storage, biology, ion exchange, and functional materials.[9] In particular, metal phosphonates have recently emerged as a class of promising catalysts or catalyst-supports for a wide range of chemical reactions, including asymmetric hydrogenations,[10] diverse oxidations,[11] polymerizations,[12] Aldol and Knoevenagel condensations,[13] and so on. Very recently, a porous zirconium-phytic acid hybrid had been prepared and used as the efficient catalyst for Meerwein-Ponndorf-Verley reductions.[14]

Inspired by these achievements, we designed a novel Nb-containing heterogeneous catalyst, niobium phytic, by using phytic acid as the building blocks. The niobium phytic was formed by the coordination between Nb^{5+} and the phosphate groups in phytic acid. As examples of applications, the synthesized niobium phytic was used as an effective heterogeneous acid-catalyst for both cyanosilylation of carbonyl compounds and dehydration of carbohydrates to form 5-hydroxymethylfurfural (HMF), which are typical acid-catalyzed reactions. The as-prepared niobium phytic showed high catalytic activity for the two reactions. In addition,

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x niobium phytic can be easily recovered and reused without considerable decrease in catalytic activity for both reactions. Phytic acid, as building blocks, has great potential in the preparation of functional heterogeneous catalysts.

Results and discussion

Catalyst characterization

The synthetic procedure for niobium phytic was presented in detail in the Experimental section. The powder XRD pattern of the synthesized niobium phytic was shown in Fig. 1a. It could be seen that the catalyst had no X-ray crystal structure. Furthermore, the XRD pattern showed one broad diffraction peak, indicating that the obtained catalyst was amorphous. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) demonstrated that the catalyst was formed from particles with a size of about 60 nm (Figs. 1b and 1c).

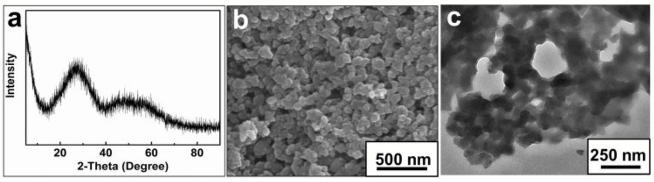


Fig. 1. Powder XRD patterns (a), SEM image (b) and TEM image (c) of the prepared niobium phytic.

The Fourier transform-infrared (FT-IR) technique was also used to characterize the synthesized catalyst (Fig. 2). The band at 3400 cm^{-1} and 1630 cm^{-1} can be associated to the surface-adsorbed molecular water.[15] It could be found that there was one band at 1020 cm^{-1}, suggesting the formation of Nb-O-P networks in the synthesized catalyst. An additional strong band was also found at 625 cm^{-1}, which was assigned to Nb-O stretching modes.[14] UV-Vis analysis for niobium phytic and Nb_2O_5 found that they had similar spectra (Fig. S1), which indicated that Nb^{5+} in niobium phytic had similar coordination pattern with Nb_2O_5.

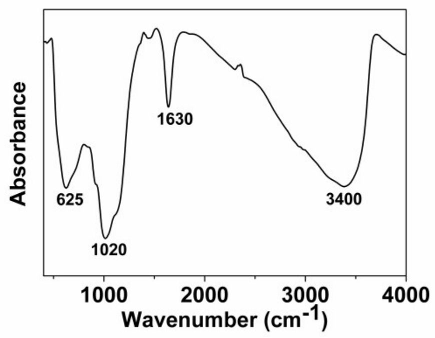


Fig. 2. FT-IR spectra of niobium phytic.

X-ray photoelectron spectroscopy (XPS) was taken to investigate the chemical state of the prepared catalyst (Fig. 3). As shown in Fig. 3a, the Nb 3d signal in niobium phytic was composed of two single peaks located at 207.5 eV for Nb $3d_{5/2}$ and 210.2 eV for Nb $3d_{3/2}$, which were characteristic of Nb^{5+}.[16] The binding energy of P 2p at 133.6 eV was characteristic of P^{5+} (Fig. 3b). These results suggested the presence of Nb^{5+} and P^{5+} in the prepared catalyst.

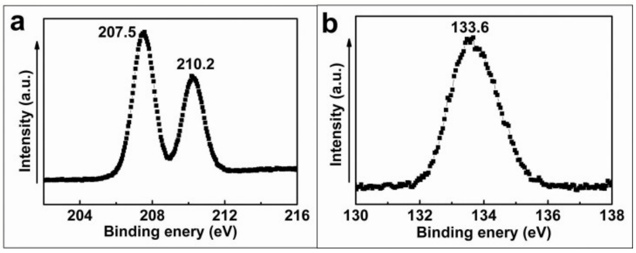


Fig. 3. The XPS spectra of Nb 3d (a) and P 2p (b) in the niobium phytic.

The textural parameters of the synthesized niobium phytic were investigated by the N_2 adsorption-desorption method after the sample was degassed at 100 °C for 24 hours. It can be seen that the N_2 adsorption-desorption isotherm of the catalyst was similar to the type IV mode, showing pore condensation with pronounced adsorption-desorption hysteresis (Fig. 4). The result in Fig. 4 indicates that the niobium phytic prepared was porous. The porosity of niobium phytic could result from the networks formed by the coordination between Nb^{5+} and phytic acid. XRD pattern (Fig. 1a) indicated that niobium phytic was poorly ordered. Therefore, it can be deduced that there were many irregular connectivity in niobium phytic, which was consistent with the fact that the pore size distribution was relatively wide (Fig. 4). The average pore diameter, the Brunauer-Emmett-Teller (BET) surface area, and the pore volume calculated from the N_2 adsorption-desorption were 12.4 nm, 30.9 m^2g^{-1}, and 0.11 cm^3g^{-1}, respectively.

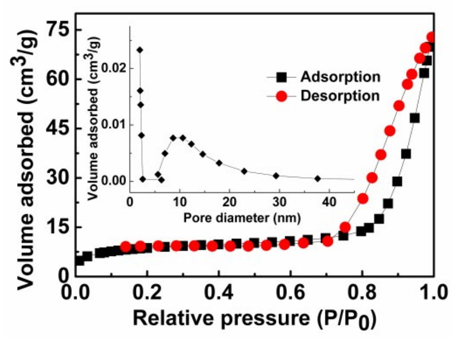


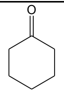
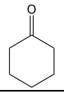
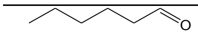
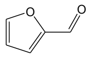
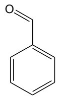
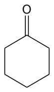
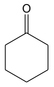
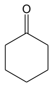
Fig. 4. N_2 adsorption-desorption isotherm for the synthesized niobium phytic.

Examination of catalytic activity

The as-prepared niobium phytic may find wide-ranging applications in different fields. It is very stable and is not soluble in water and common organic solvents, which are the excellent characteristics of heterogeneous catalysts. Generally speaking, Nb-containing compounds could be used as acid catalysts for various organic reactions. As examples of applications, we used the niobium phytic as a heterogeneous catalyst to catalyze both cyanosilylation of carbonyl compounds and dehydration of carbohydrates to form 5-hydroxymethylfurfural (HMF), which are both acid-catalyzed reactions.

Cyanosilylation of carbonyl compounds is a convenient reaction to synthesize cyanohydrins, which are important intermediates in the synthesis of fine chemicals and pharmaceuticals.[17] The synthesized niobium phytic was used as a heterogeneous catalyst for the cyanosilylation reaction of carbonyl compounds, including various aldehydes and ketones, with trimethylsilyl cyanide (TMSCN) to produce cyanohydrins, and the results are given in Table 1. It is obvious that the reaction did not proceed without any catalyst (Table 1, entry 1). To our delight, the niobium phytic catalyst showed excellent performance for the cyanosilylation reactions at room temperature. We also studied the activity of commercial Nb_2O_5 for the cyanosilylation of cyclohexanone (Table 1, entry 6), and the activity was lower than the as-prepared niobium phytic (Table 1, entry 2). The higher activity of niobium phytic could be caused by its higher acidity and lower crystallinity, which will be discussed in detail in the following section. The reusability of the as-prepared niobium phytic for the cyanosilylation reaction of cyclohexanone was also studied. It was indicated that the catalyst could be reused at least five times without reducing the catalytic activity, as shown in Fig. 5. The niobium phytic recovered after reused five times was characterized by FT-IR, XRD, XPS, SEM, and TEM. As shown in the patterns of FT-IR (Fig. 6a), XRD (Fig. 6b), and XPS (Figs. S2 and S3), it can be seen that the recovered catalyst showed the characteristics peaks, which indicated that the structure of the recovered catalyst was not changed. Meanwhile, from the images of SEM (Fig. 6c) and TEM (Fig. 6d), it is obvious that the recovered catalyst did not collapse and the particle showed no obvious aggregations compared with the fresh catalyst. XPS examinations showed that the concentrations of Nb, P, C and O on the surface of fresh and used niobium phytic were not nearly changed (Table S1) after five catalytic recycles. Further, the thermogravimetric analysis in this work indicated that the decomposition temperature of the as-prepared catalyst was about 300 °C (Fig. S4), which was much higher than the reaction temperature. The above examinations proved that niobium phytic was stable in the catalytic process and its properties were not changed noticeably after used.

Table 1. Cyanosilylation reaction of carbonyl compounds using TMSCN.[a]

Entry	Reactant	Catalyst	Reaction time (min)	Yield (%)[b]
1		None	20	0
2		Niobium phytic	20	98
3		Niobium phytic	15	96
4		Niobium phytic	15	100
5		Niobium phytic	15	98
6		Commercial Nb_2O_5	30	16
7		Phytic acid	20	13[c]
8		Amorphous Nb_2O_5[d]	30	37

[a] Reaction conditions: carbonyl compound, 2 mmol; TMSCN, 4 mmol; catalyst, 0.1 g; CH_2Cl_2, 4 g. [b] Yields were determined by GC using ethylbenzene as the internal standard. [c] The conversion of cyclohexanone was 18% and the selectivity was about 72% with some unidentified by-products. [d] The amorphous Nb_2O_5 was prepared by hydrolysis of niobium(V) ethoxide.

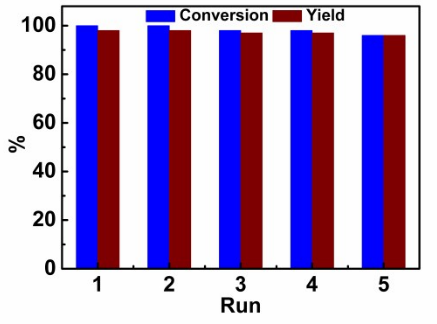


Fig. 5. Reusability of niobium phytic for the cyanosilylation reaction of cyclohexanone. Reaction conditions: cyclohexanone, 20 mmol; TMSCN, 40 mmol; niobium phytic, 0.1 g; CH_2Cl_2, 4 g, reaction time, 15 min; reaction temperature, room temperature.

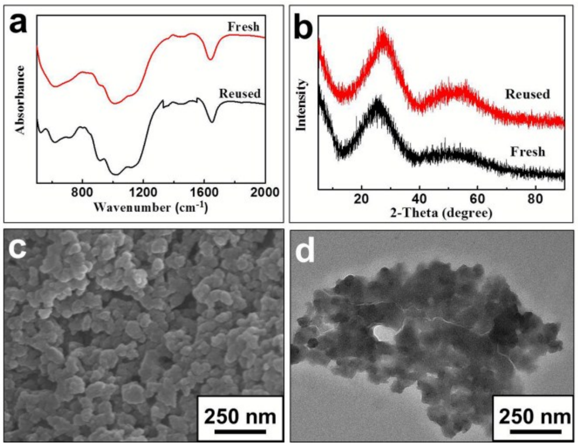


Fig. 6. The characterization of niobium phytic after reused five times. FT-IR spectrum (a), XRD pattern (b), SEM image (c), and TEM image (d).

We also used the niobium phytic as an acidic heterogeneous catalyst for dehydration of carbohydrates to form HMF in the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), which is a very important reaction for biomass conversion.[18] We conducted the reaction using the synthesized niobium phytic, $NbCl_5$, and commercial Nb_2O_5 as the catalysts at the same reaction conditions, and the results are shown in Table 2. Although the dehydration of fructose could be proceeded without catalysts in [Bmim]Cl, the yield of HMF was very low (Entry 1, Table 2), indicating that the catalyst was necessary to achieve high reaction activity. It was found that niobium phytic showed the highest HMF yield (87.5%) (Entry 2, Table 2) with full conversion of fructose. In contrast, although the conversion of fructose was also 100% over $NbCl_5$, the yield of HMF was only 73.6% (Entry 3, Table 2) due to the side reaction. When using Nb_2O_5 as the catalyst, longer reaction time (1.5 h) was needed to convert fructose completely (Entry 4, Table 2). But, the yield of HMF was still lower than the result obtained over niobium phytic because longer reaction time could cause side reactions of HMF. These results indicated that niobium phytic was the better catalyst for dehydration of fructose, which was comparable with many results reported in the literatures using heterogeneous catalysts in various solvents.[17] Recyclable experiments indicated that niobium phytic could also be reused five times for the dehydration of fructose with a slight reduction in catalytic efficiency. The slight decrease in catalytic activity maybe resulted from the leaching of Nb (about 21 ppm) in the reaction mixtures due to the strong solvent power of [Bmim]Cl, which could be examined by ICP method. Furthermore, the niobium phytic could also be used to catalyze the dehydration of inulin and sucrose in [Bmim]Cl to produce HMF, and yields of 56.4% and 45.4% (Entries 5 and 6, Table 2), respectively, could be obtained with a prolonged reaction time (3 h). Compared with fructose, inulin and sucrose only gave moderate HMF yields. There were two reasons for this phenomenon. Firstly, the reaction process of inulin and sucrose to produce HMF was a two-step reaction involving hydrolysis and dehydration, which could increase side reactions and thus lowered the reaction yield. Secondly, there were glucose units in the structure of inulin and sucrose and the niobium phytic showed no activity for glucose. After the reaction, glucose was remained detected by HPLC with a refractive detector (Shimadzu RID-10A). Only fructose units could be converted into HMF over niobium phytic, and thus HMF yield was moderate when inulin and sucrose were used as the substrates.

Table 2. Dehydration of carbohydrates to produce HMF.[a]

Entry	Reactant	Catalyst	Time (h)	Conversion (%)	Yield (%)[b,c]
1	Fructose	None	1	18.4	12.7(±1.3)
2	Fructose	Niobium phytic	1	100	87.5(±1.9)
3	Fructose	$NbCl_5$	1	100	73.6(±4.5)
4	Fructose	Nb_2O_5	1	90.5	76.8(±2.6)
			1.5	100	81.6(±1.7)
5	Fructose	Niobium phytic (5th)[d]	1	97.8	74.3
6	Inulin	Niobium phytic	3	100	56.4(±2.9)
7	Sucrose	Niobium phytic	3	100	45.4(±3.5)

[a]Reaction conditions: reactant 0.1 g; catalyst 0.1 g; [Bmim]Cl 1 g; reaction temperature 100 °C. [b]The yields were determined by HPLC using an external standard method. [c]The data in parentheses was the error bars. [d]The niobium phytic was resued for the fifth time.

Explanation of the higher catalytic activity of niobium phytic

As discussed above, niobium phytic showed higher activity for the two examined reactions than Nb_2O_5, which was induced by two possible reasons, including higher acidity and lower crystallinity. Firstly, we determined the local environment of the Nb species in niobium phytic and Nb_2O_5 by XPS method of Nb 3d. As shown in Fig. 7a, the binding energy values of Nb in niobium phytic corresponding to Nb $3d_{5/2}$ and Nb $3d_{3/2}$ were 207.5 and 210.2 eV, which were higher than the results of Nb_2O_5 (207.2 and 209.9 eV). The higher binding energy of Nb 3d in niobium phytic caused by that the formation of P-O-Nb bonds in its structure could result in a higher positive charge on Nb atoms, which could increase the acidity of Nb.[19] Further, the acidity of niobium phytic and commercial Nb_2O_5 was examined by NH_3-TPD method. As shown in Fig. 7b, niobium phytic showed a peak at about 220 °C, which was related to the weak acid sites (mainly resulted from Nb^{5+}). However, commercial Nb_2O_5 showed no obvious peaks. The results in Fig. 7b indicated that the amount of NH_3 desorbed from niobium phytic was much more than commercial Nb_2O_5, which was consistent with their acidity. We also conducted the pyridine absorption FT-IR analysis to identify the kind and number of acid sites for niobium phytic and Nb_2O_5 (Fig. 7c). From the figure, we could see that the characteristic of Lewis acid sites at about 1606 and 1445 cm^{-1} were observed in the spectra of both niobium phytic and Nb_2O_5.[20] The number of Lewis acid sites in niobium phytic was about 196 μmol/g, which was higher than that in Nb_2O_5 (78 μmol/g). The band at about 1487 cm^{-1} is normally attributed to a combination band associated with both Brønsted acid and Lewis acid sites.[21] Meanwhile, a band of about 1540 cm^{-1} existed in the spectra of niobium phytic, which was the characteristic of Brønsted acid site.[22] This Brønsted acid site was resulted from the small amount of P-OH species of the phosphate groups,[23] which did not coordinate with Nb^{5+}. In contrast, Nb_2O_5 showed no characteristic of Brønsted acid site. The Brønsted acid sites existed in niobium phytic could also promote the reactions. However, when phytic acid was used as the catalyst for the cyanosilylation reaction of cyclohexanone, the yield of the desired product was only 13% with a selectivity of about 72% (Entry 7, Table 1). This result indicated that the Lewis center (Nb) was very crucial for the high catalytic activity of niobium phytic. Therefore, based on the results obtained from XPS, NH_3-TPD and pyridine absorption FT-IR examinations, it can be concluded that the acidity of niobium phytic is much stronger than commercial Nb_2O_5. Because the two examined reactions were both acid-catalyzed reaction, the higher acidity of niobium phytic was beneficial to increase the rate of the two reactions.

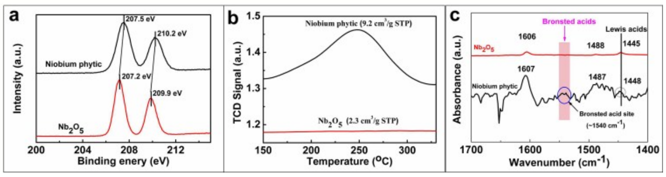


Fig. 7. XPS of Nb 3d (a), NH_3-TPD spectra (b), and pyridine absorption FT-IR analysis (c) for niobium phytic and Nb_2O_5.

Lower crystallinity was another reason for the higher activity of niobium phytic. Niobium phytic synthesized and commercial Nb_2O_5 were characterized by XRD (Fig. 8). It is obvious that the synthesized niobium phytic was amorphous with a very low crystallinity. In contrast, commercial Nb_2O_5 showed better crystallinity. The lower crystallinity of niobium phytic could be favourable for the reactants to contact with the acid center (Nb) of the catalyst, and thus promoted the reaction with a higher activity. It was found that an amorphous Nb_2O_5 (Fig. 8) prepared by hydrolysis of niobium(V) ethoxide, which had similar acidity with commercial Nb_2O_5 (Fig. S5), showed better catalytic activity (Entry 8, Table 1) for cyanosilylation reaction of cyclohexanone than the commercial Nb_2O_5, which indicated that lower crystallinity was indeed beneficial to the reaction. In addition, as shown in Table S2, niobium phytic had higher BET surface area, larger pore diameter, and larger pore volume than commercial Nb_2O_5, which were also helpful to increase the diffusion of reactants to the activity center to promote the reactions proceed. Lower crystallinity combined with higher acidity together resulted in the higher catalytic activity of niobium phytic.

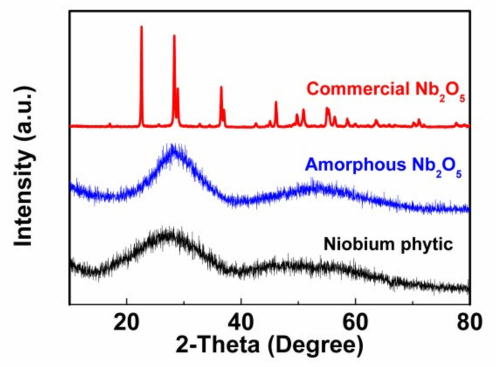


Fig. 8. XRD patterns of niobium phytic, commercial Nb_2O_5, and amorphous Nb_2O_5 prepared by hydrolysis of niobium(V) ethoxide.

Conclusions

In summary, a functional heterogeneous acid catalyst, niobium phytic, could be designed using phytic acid as the building block to react with $NbCl_5$. It was discovered that niobium phytic showed very high activity for both cyanosilylation of carbonyl compounds with TMSCN and dehydration of carbohydrates to produce HMF, which are both acid-catalyzed reactions. Niobium phytic could be easily recovered and reused at least five times without decreasing the reaction activity and selectivity. Further study indicated that niobium phytic had higher activity than commercial Nb_2O_5, which could be resulted from the higher acidity and lower crystallinity of niobium phytic. The findings in this work provide the view of designing new functional catalyst derived from naturally-occurred building blocks for various organic reactions.

Experimental

Materials

Fructose (99%), sucrose (99%) and 1-hexaldehyde (>95%) were purchased from Alfa Aesar. Inulin (95%), Nb_2O_5 (99.5%), niobium (V) chloride (99+%), trimethylsilyl cyanide (TMSCN, 97%) and furfural (98%) were provided by J&K Scientific Ltd. N,N-Dimethylformamide (DMF), CH_2Cl_2, ethyl ether, ethanol, methanol and cyclohexanone were A. R. grade and were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. Phytic acid with C. P. grade was received from Sinopharm Chemical Reagent Beijing Co., Ltd. Here, we needed to point out that phytic acid should be obtained from seeds and grains of plants.[8] However, in this work, we mainly focus on the preparation of functional catalysts using phytic acid as the building blocks and thus we purchased it from chemical company. The ionic liquid [Bmim]Cl used in the experiment were purchased from Lanzhou Greenchem ILs, LICP, CAS, China (Lanzhou, China) with a purity over 99.9%. [Bmim]Cl was dried at 80 °C under vacuum for 96 h before use.

Synthesis of niobium phytic

Niobium chloride (the resource of Nb^{5+}, 22 mmol) and phytic acid (the ligand, 10 mmol) were dissolved in DMF (400 mL) in a flask of 1000 mL. Then, triethylamine (the deprotonation reagent, 150 mmol) was added into the solution dropwisely with a time of 3 h. After that, the mixture was firstly stirred for 5 h at room temperature and then aged under static conditions at 80 °C for 6 h. Finally, the white precipitate was separated by filtration, thoroughly washed with DMF to remove the unreacted $NbCl_5$ and phytic acid. Before the characterization and utilization, the sample was washed by ethanol at 90 °C through Soxhlet extraction for 72 h to remove DMF completely. After that, the niobium phytic was dried at 80 °C under vacuum for 12 h. The yield of niobium phytic was about 89% (7.85g). ICP analysis showed that the Nb/P molar ratio in niobium phytic was about 1:3. Anal. Found: 21.27% Nb, 23.59% P, 9.13% C. Calcd. for $Nb_2P_6C_6O_{24}H_8$ (835.77): 22.23% Nb, 22.23% P, 8.62% C.

Cyanosilylation of carbonyl compounds

In a typical experiment, carbonyl compound (2 mmol), TMSCN (4 mmol), CH_2Cl_2 (4 g) and catalyst (0.1 g) were charged into a flask of 10 mL equipped with a magnetic stirrer. The reaction mixture was stirred at room temperature with a desired reaction time. After the reaction, the products were analyzed by gas chromatography (GC, Agilent 7890) using ethylbenzene as the internal standard, and identification of the products was done by GC-MS (Shimadzu QP2010). In the experiments to test the reusability of niobium phytic, the catalyst was recovered by centrifugation, washed using ethanol and ethyl ether. After drying under vacuum at 80 °C for 12 h, the catalyst was reused for the next run by adding new reactants and solvents.

Dehydration of carbohydrates to produce HMF

In a typical experiment, carbohydrate (0.1 g), catalyst (0.1 g) and [Bmim]Cl (1 g) were charged into a flask of 5 mL equipped with a magnetic stirrer. The mixture was stirred at 100 °C for the desired time. Then the mixture was cooled to room temperature immediately. The amount of HMF was analyzed by HPLC using an external standard method with Shimadzu LC-15C pump, Shimadzu UV-Vis SPD-15C detector at 282.0 nm, and a Supelcosil LC-18 5ìm column at 35 °C. Before analyzed, the reaction mixture was diluted to 1000 mL. Methanol/water solution (50/50 V/V) was used as the mobile phase at a flow rate of 0.8 mL/min.

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Notes and references

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Graphical abstract

Niobium phytic, designed from phytic acid and $NbCl_5$, showed high activity for cyanosilylation of carbonyl compounds and dehydration of carbohydrates.